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Title: HIGH TEMPERATURE OXIDATION OF BERYLLIUM MODIFIED INTERMETALLIC COMPOUNDS OF THE NIOBIUM-CHROMIUM SYSTEM

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Abstract

Intermetallic compounds based on the Laves phases $NbCr_2$ and $TiCr_2$ are of interest for high temperature applications. At temperatures where the high temperature strength and creep resistance of these compounds are excellent, their oxidation resistance is relatively poor. Beryllide compounds in the Cr-Be, Ti-Be and Nb-Be systems ($CrBe_2$, $TiBe_{12}$, $TiBe_2$, $NbBe_{12}$) on the other hand, exhibit excellent oxidation resistance even at temperatures in excess of 1200° C, due to the formation of protective BeO scales. The pure beryllides have relatively poor mechanical properties however. Therefore we have attempted to improve the oxidation resistance of the Nb-Cr-Ti based Laves phases using alloying additions of beryllium. Alloys investigated include $CrBe_2$, $NbBe_2$ and $NbCr_2$ with 10, 25, and 33 atomic percent beryllium substituted for Cr. We have determined that there is a significant solubility of Be in $NbCr_2$. Beryllium modified $NbCr_2$ exhibits protective oxidation, with the growth of scales containing principally Cr_2O_3, and BeO.

Introduction

Perhaps the first issue which must be addressed in any study of beryllium alloy development is the rationale for the study itself. This is particularly important given the well known toxicity of beryllium compounds. It must be pointed out that this research was conducted in laboratories dedicated to the investigation of beryllium alloys. This type of work should only be conducted in facilities which have been designed for the purpose, such as those at LANL. In any case, the rationale for investigating the oxidation of beryllium alloys is straightforward; Beryllium forms a protective oxide, BeO, which has two allotropes of which only the α-phase is usually observed. The high temperature oxidation kinetics of beryllium compounds are similar to those exhibited by the other nominally protective oxide forming alloys, i.e. those which contain sufficient quantities of aluminum or chromium (1). Among the beryllides are some of the highest melting intermetallic compounds as well as some of the lowest density refractory metallic phases with densities on the order of 2-4 gm/cc. Beryllium forms intermetallic compounds with all of the transition metals (except those of group IB), all of the other group IIA elements, as well as all of the lanthanides and light actinides. The majority of the compounds are

quite complex (e.g. MBe_{13} (Fm3c , $NaZn_{13}$ prototype) and M_2Be_{17} (R3m, Nb_2Be_{17} prototype)) but there are also simpler structures such as NiBe (B2) and Laves phases (e.g. $MnBe_2$-C15, $CrBe_2$- C14) (2). These relatively simple compounds are arguably the most likely to have any potential as structural alloys insofar as they do at least appear to have some potential for ductility and toughness. Perhaps more importantly, the formation of beryllide phases similar to other more extensively investigated intermetallics suggests that there may be some mutual solubility in these systems (e.g. NiBe-NiAl, $NbCr_2$, $NbBe_2$, $CrBe_2$). Furthermore, the relatively small size and rapid self diffusion coefficient of beryllium suggests that the activity of beryllium may be sufficiently high at even rather low concentrations of Be that it might relatively easily diffuse to the metal oxide interface and maintain the protective beryllia scale on alloys which otherwise might not form protective scales. Finally, the potential for formation of protective dual oxide scales (i.e. spinels) has very rarely been achieved. Beryllium, however, forms phases such as chrysoberyl ($BeO-Al_2O_3$) with both alumina and chromia, which may actually be more protective than the binary oxides as it is in fact a higher density phase. These principles were successfully applied in our investigations of the B2 Ni(Al, Be) system(3). In recent years there has been a number of studies of alloys based on $NbCr_2$. The most successful of these have actually been two or more phase alloys with the intermetallic compound present as a discontinuous phase in a BCC matrix based on either Cr, Ta, or Nb, with additions of Ti in some cases in order to improve high temperature strength and ductility (4-8). The base material for this study is the Laves phase $NbCr_2$. Although the aforementioned studies have demonstrated the viability of the two phase alloys, in the present case we choose to start by surveying the oxidation of materials based simply on the substitution of Be for Cr in the $NbCr_2$ compound. This approach allows us to investigate the concentration of Be required to result in any possible improvement of the oxidation of this compound as well as the solubility of Be in $NbCr_2$, which is needed in order to understand the potential for modifying mechanical properties by this route.

We have previously investigated the oxidation of single phase $CrBe_2$ and observed excellent oxidation resistance with some indication that the phase $CrBeO_4$ (a chrysoberyl type phase) was formed in addition to BeO (9). In this work we were concerned with the possibility of observing a transition from Cr_2O_3 formation to the growth of scales containing either $CrBeO_4$ and/or BeO. If this in fact did occur, than it might be the case that a minimum in the oxidation rate was observed at some intermediate composition or that the maximum useful exposure temperature of the alloy might be greater than that of $NbCr_2$ (4,5). Earlier experiments with beryllium modified $NbCr_2$ (containing 1-2 atomic percent (a/o) Be substituted for Cr) had observed non-adherent scales associated with the evaporation of Cr_2O_3 at high temperatures (9). In the present investigation we therefore concentrated on alloys containing higher levels of Be in the hope that these would form BeO if not $CrBeO_4$. Alloys investigated include in this study were $NbBe_2$ and $NbCr_2$ with 10, 25, and 33 atomic percent beryllium substituted for Cr.

Experimental

The alloys were prepared by arc-melting and casting high-purity elemental material. Specimens were cut from the ingot using electro-discharge machining (EDM) and the surfaces were prepared by grinding to a 1000 grit finish. One sample of each alloy was mounted in epoxy and polished for metallographic examination. Homogeneity was checked using powder XRD, optical and scanning electron microscopy. Additional

phases were identified in some of the alloys with higher beryllium contents; these are shown in table 1 below. Samples were placed into a tube furnace and given an isothermal exposure at peak temperatures of 800, 900, 1000, 1100 or 1200°C for 16 hours in laboratory air. For safety, the tube furnace was closed and compressed air passed through the furnace at approximately 1 cc/s. Oxidized samples were characterized by x-ray diffraction (XRD), optical microscopy, and scanning electron microscopy (SEM). Because of the risks associated with respirable beryllium compounds, only materials which clearly developed an adherent oxide layer were analyzed in detail. Gravimetric analysis was not employed in this study as our principal interest in modifying the mechanism of oxidation via formation of beryllium oxide phases. Furthermore, the simultaneous processes of weight gain from oxide formation and/or internal oxidation and volatilization chromia which occurs at temperatures in excess of 900° C renders gravimetric techniques potentially very misleading when applied to this system.

Results

X-ray diffraction showed that the alloys containing beryllium in excess of 10 a/o contained a mixture of C14, C15 and C36 phases. Since the relative amounts of these phases will vary depending on both the equilibrium composition and the cooling rate of the sample ingots from the melt, we did not attempt to quantify phases. At 10 a/o and below, the beryllium appeared to go entirely into solution, as shown in figure 1, a plot of lattice parameter as a function of Cr/Nb ratio for alloys containing 5 and 10 a/o Be. Apparently the beryllium can substitute onto either the Nb or Cr sublattice in $NbCr_2$. At a constant Cr-content, the lattice constant decreases as Be replaces Nb. Although Be may substitute on the Cr-sublattice, and Be is smaller than Cr, the lattice constant increases. In all cases however the entire sample consisted of intermetallic Nb-Cr-Be phases with no evidence of BCC phases (Cr or Nb rich solutions).

Post exposure examination of the samples did reveal that chromia evaporation was occurring in all of the samples, as evidenced by the green deposits formed on the alumina boat and inside the tube furnace. Cross sections of the samples revealed that as the beryllium content increased a transition from external scale formation to internal oxidation occurred . This is illustrated in figures 2 and 3 below, which compare the extreme cases of the alloys $NbCr_{1.9}Be_{0.1}$ and $NbCr_{1.33}Be_{0.66}$. It is apparent in the micrograph of the cross section of $NbCr_{1.33}Be_{0.66}$ that extensive internal oxidation has occurred in this case. This is further illustrated in figure 3, where the 1200°C results are compared for all 4 alloy compositions. The very thick external scale formed at 0.1 Be gives way to almost pure internal oxidation in the 0.66 Be sample. Brady has observed internal oxidation and nitridation in Cr based alloys containing $NbCr_2$ (7). There is a layer clearly visible in the microstructure below the scale in all of the samples exposed at 1000°C and above. This has as yet not been unambiguously identified as either O or N rich. In this case the phase which is preferentially internally attacked has not as yet been identified conclusively. It is, however, rich in niobium and chromium, suggesting that it is not the beryllium containing phases which are oxidized, but rather that the secondary niobium-chromium phases (C14 and C36) which are precipitated as the equilibrium is shifted away form the single Laves phase composition which are susceptible to preferential oxidation. Given the inherent brittleness and the apparent susceptibility to internal oxidation, it is not surprising that we also observed pest reactions in some of these alloys. This was observed in a test conducted at 1000°C, wherein the tube furnace was sealed so that the alloys would be exposed to progressively lower oxygen activity.

All of the alloys containing greater than 0.1 Be exhibited some degree of disintegration in this case, with nearly complete disintegration in the case of both 0.2 and 0.5 Be samples.
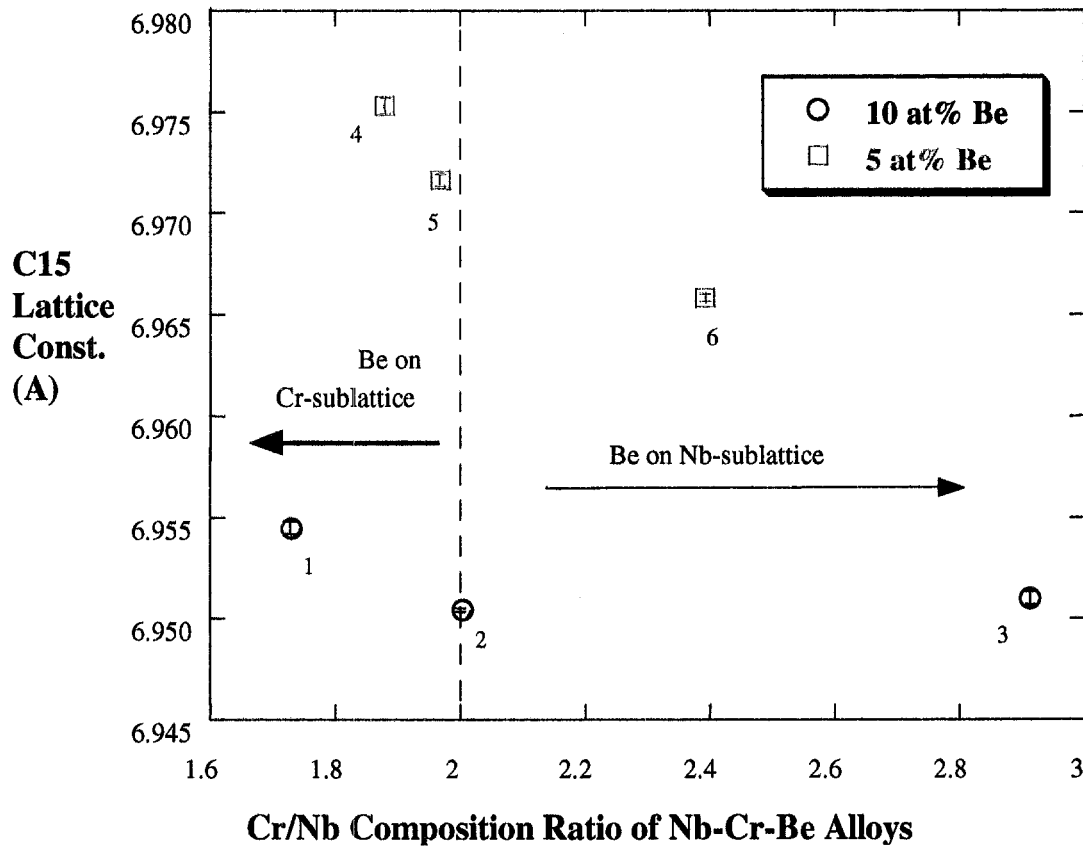

Figure1: Lattice constant of $NbCr_2$ containing 5 and 10 atomic percent beryllium. It is evident that the beryllium can and does substitute for both Nb and Cr, which suggests the possibility that it might improve ductility as well.
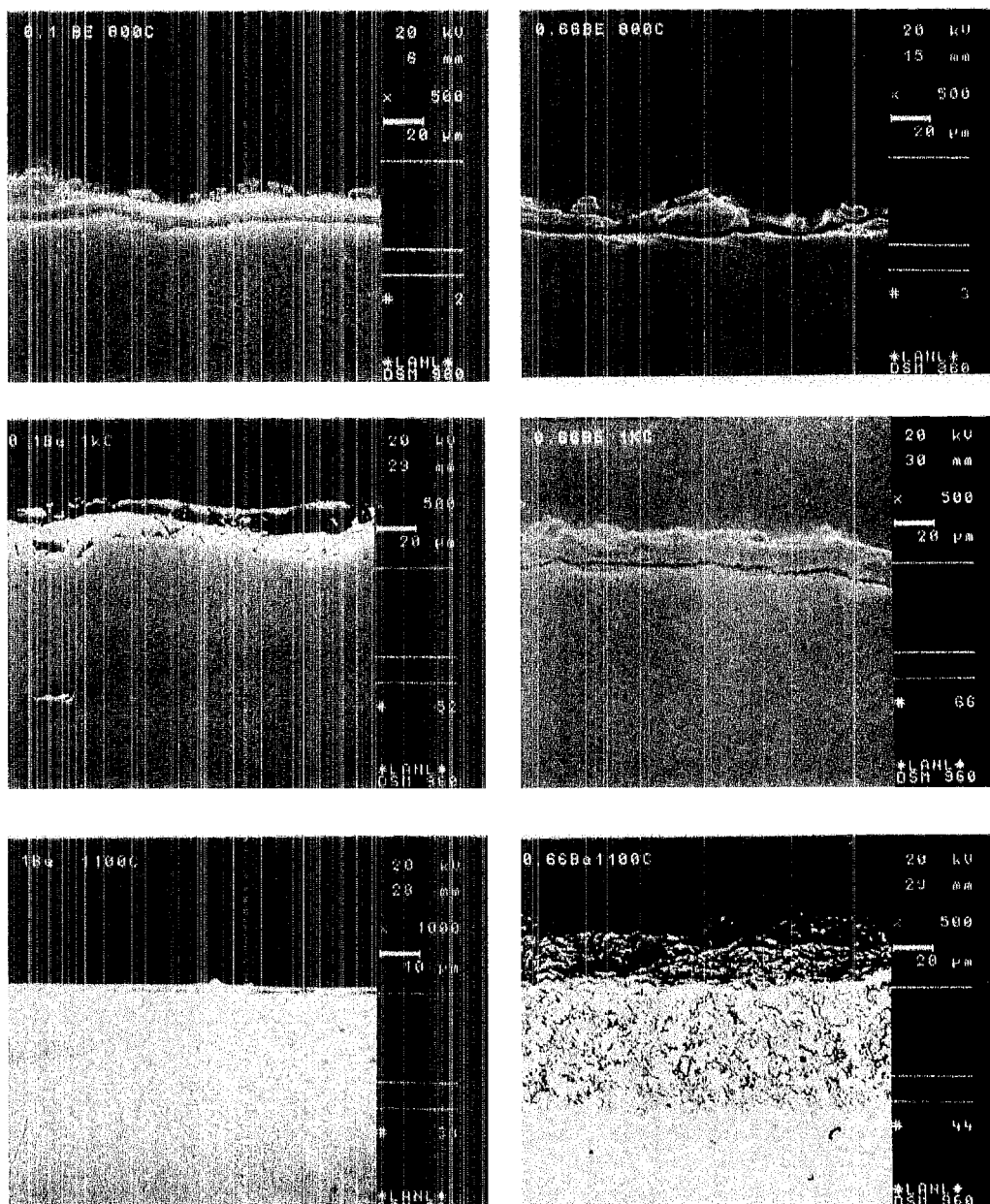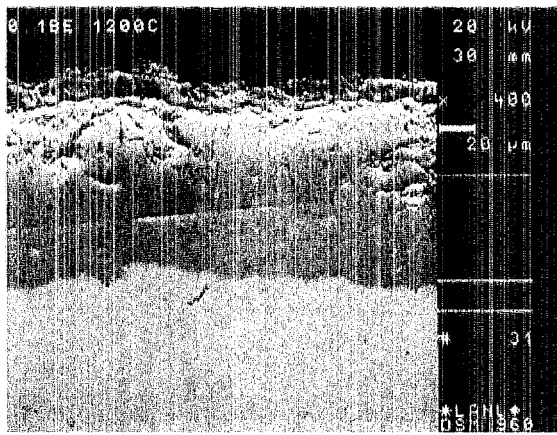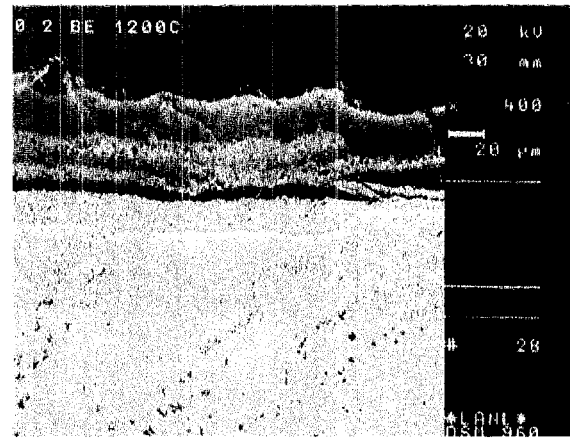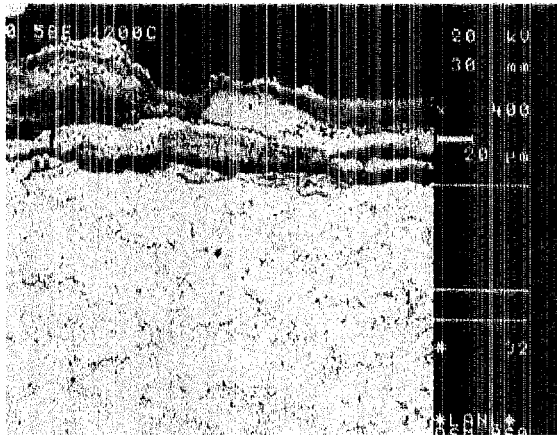
Figure 2: Comparison of the cross sections of alloys $NbCr_{1.9}Be_{0.1}$ (left) and $NbCr_{1.33}Be_{0.66}$ (right) exposed to air for 24 hours at 800, 1000, and 1100° C. There is a clear progression from principally external scale formation to extensive internal oxidation as both the temperature and beryllium content increase.
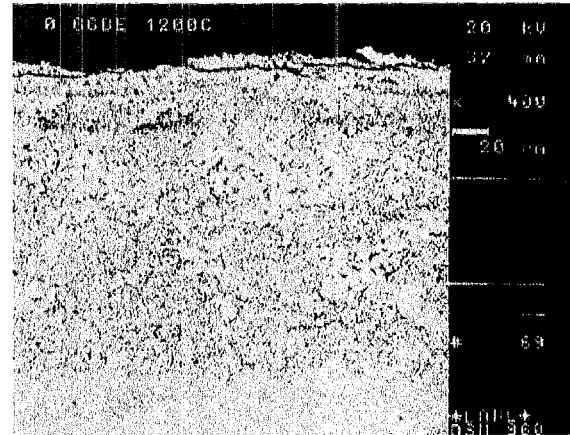
3-A) $NbCr_{1.9}Be_{0.1}$

3-B) $NbCr_{1.8}Be_{0.2}$

3-C) $NbCr_{1.5}Be_{0.5}$

3-D) $NbCr_{1.33}Be_{0.66}$

Figure 3: SEM micrographs of the cross section of each alloy investigated in this study exposed for 24 hours at 1200° C. Note once again the progressive shift from external scale formation to internal oxidation.

Conclusions and Future Work

There were two objectives to this study; to determine whether beryllium would go into solution in $NbCr_2$ and, subsequently, form beryllium oxide based scales which were more protective than chromia. The first point was well proven. Beryllium was shown to substitute for both Nb and Cr in $NbCr_2$ at compositions up to $NbCr_{1.9}Be_{0.1}$. At higher beryllium contents, multiple phases were observed, albeit all of them refractory intermetallic phases so that while these higher beryllium content compounds are considerably more complicated than we might desire, they can still be expected to act as effective beryllium and chromium reservoirs in BCC matrix alloys. Beryllium modified $NbCr_2$ did in fact develop protective scales, (containing a of Cr_2O_3, BeO, $NbCr_2O_5$ and $CrBeO_4$ among other mixed oxides) however, as the Be content increased a transition to internal oxidation was observed. This latter effect suggests that in the BCC matrix alloys the lower Be content phases might be preferable. Pest oxidation was also exhibited by some of the beryllium modified alloys. This latter effect, while interesting, does not in itself eliminate these alloys from consideration as the pest phenomenon is not generally

observed in ductile alloys. In any case, the next obvious step is to further investigate additions near x=0.1 (~6 a/o) using thermogravimetric analysis in order to quantitatively determine the optimum composition (defined by a minimum in the oxidation rate) . The higher beryllium content compounds may still be viable in the BCC/Laves phase composite alloys. Inspection of the ternary Nb-Cr-Be system suggests that these alloys should be first investigated in the Cr rich corner of the system, since the numerous higher beryllides in the Nb-Be system may complicate the objective of dissolving the beryllium principally in the Laves phase.

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